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# Reactions of cyclomanganated complexes with carbon disulfide: routes to $\eta^2$-aryldithiocarboxylate-$Mn(CO)_4$ complexes and to the trithiocarbonate complex $(\mu_3\text{-}CS_3)_2Mn_4(CO)_{16}$.

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## Abstract

Reaction of cyclomanganated aryl ketones with $CS_2$ proceeds with insertion into the Mn-C bond to give $\eta^2$-dithiocarboxylato-$Mn(CO)_4$ compounds. With other cyclomanganated substrates such as that from $Ph_3P{=}S$, and also with $Mn_2(CO)_{10}$ , $CS_2$ gives $(\mu_3\text{-}CS_3)_2Mn_4(CO)_{16}$ with bridging trithiocarbonate ligands.

## 1. Introduction

There is now a well-developed chemistry of cyclomanganated complexes [1]. These compounds are readily formed from aromatic and heteroaromatic ketones [2], from substrates with imine or amine donor groups [3], from triphenyl-phosphine or -arsine chalcogenides [4], and from chalcones [5] to give, for example, compounds **1-3**.

[Diagrams 1-3 near here]

The Mn-C bond of these species is a site of reactivity, and combination with alkenes [6], alkynes [7], organoisocyanates [8], sulfur dioxide [9] or mercuric chloride [10] have all been shown to generate novel derivatives. For many of these reactions the first step in the process is undoubtedly insertion of the substrate into the Mn-C bond, followed by rearrangement with or without demanganation.

Another molecule that is known to insert into M-C bonds (as well as into M-H, M-O, M-P or M-S bonds) is $CS_2$ [11]. This generally leads to the formation of bidentate dithiocarboxylate complexes (e.g. $MeCS_2Mn(CO)_4$ from $MeMn(CO)_5$ [12]), although monodentate species sometimes form (e.g. $PtCl(SC(S)H)(PPh_3)_2$ from $Pt(H)(Cl)(PPh_3)_2$ [13]. The only previous investigation involving cyclometallated substrates that we are aware of is the reaction of a nickel complex to give, initially, a *gem*-dithiolate complex which reacted further to give a $\eta^2$-trithiocarbonate complex and a thioketone (eqn 1) [14].

[Equation 1 near here]

We now report the reactions of $CS_2$ with a range of cyclomanganated complexes.

## 2. Experimental Section

### *2.1 General*

All manipulations were carried out in an oxygen-free $N_2$ atmosphere with dried solvents in standard Schlenk equipment or on a standard vacuum line. Orthomanganated substrates were prepared by published methods [2-5], while $CS_2$ was purified by trap-to-trap distillation on the vacuum line.

### *2.2 Instrumentation.*

Infrared spectra were recorded on a Digilab FTS-40 FTIR spectrophotometer. NMR spectroscopy was performed using a Bruker DRX400 Avance in $CDCl_3$; assignments were based on standard 2-D experiments. Routine electrospray mass spectra (ESMS) were obtained on a VG Platform II spectrometer operating under standard conditions in MeOH. Na[OMe] was added as an ionisation aid [15]. Elemental analysis was performed by the Campbell Microanalytical Laboratory, University of Otago. Melting points were measured on a Reichart Thermopan melting point apparatus and are uncorrected.

### *2.3 Reactions.*

### *2.3.1 Reaction of $\eta^2$-(2-acetyl-5-methoxyphenyl)tetracarbonylmanganese with $CS_2$.*

The cyclomanganated ketone **1** (133 mg, 0.42 mmol) was placed in a thick-walled glass ampoule (*ca* 20 mL capacity). This was attached to a vacuum line, evacuated, and $CS_2$ (*ca* 10 mL) was distilled in. The ampoule was sealed under vacuum and transferred to a Carius tube where it was heated at 85°C for 24 h. When the cooled ampoule was stored at -20°C for 72 h orange crystals formed. The ampoule was opened and the crystals were collected, and characterised as $\eta^2$-(2-acetyl-5-methoxyphenyldithiocarboxylato)tetracarbonylmanganese, **4**, (91 mg, 55%). Mp 116°C. Found: C 44.2; H 2.3%. Calc. for $C_{14}H_9MnO_6S_2$: C 42.9; H 2.3%. IR: ν(CO) ($CH_2Cl_2$) 2093 (m), 2016 (vs), 2002 (vs),1963 (s) $cm^{-1}$; $^1$H NMR: δ 7.59 (1H, d, $^3J_{H\text{-}H} = 8.6$ *Hz*, H3), 7.02 (1H, dd, $^3J_{H\text{-}H} = 8.5$ *Hz*, $^4J_{H\text{-}H} = 2.2$ *Hz*, H4), 6.95 (1H, d, $^4J_{H\text{-}H} = 2.1$ *Hz*, H6), 3.92 (3H, s, $OCH_3$), 2.59 (3H, s, $C(O)CH_3$). $^{13}$C NMR: δ 199.2 (C7), 161.9 (C5), 149.2 (C1), 131.2 (C3), 129.6 (C2), 116.1 (C4), 113.0 (C6), 56.2 ($O\underline{C}H_3$), 29.6 ($C(O)\underline{C}H_3$); ESMS: (MeOH with added Na[OMe], cone voltage 20 V), m/z 423 (33%) $[M+OMe]^-$; 395 (100%) $[M+OMe-CO]^-$; 363 (48%) $[M-H-CO]^-$; 589 (28%) $[2M-Mn(CO)_5]^-$. This compound was also characterised by an X-ray crystal structure determination; see below.

### *2.3.2 Reaction of $\eta^2$-(2-benzoylphenyl)tetracarbonylmanganese with $CS_2$.*

Cyclomanganated benzophenone (190 mg, 0.55 mmol) was reacted with $CS_2$ (*ca* 10 mL) in a sealed ampoule at 85°C for 24 h, following the same procedure as above. The cooled ampoule was opened and the excess $CS_2$ removed under vacuum. The residue was chromatographed on an alumina column, with diethyl ether: petroleum spirits (1:1). The first fraction eluted gave a dark orange oil which did not crystallise. This was characterised as $\eta^2$-(2-benzoyl-phenyldithiocarboxylato)tetracarbonylmanganese, **5**, (156 mg, 67%). IR: ν(CO) ($CH_2Cl_2$) 2093 (m), 2019 (vs), 2007 (vs), 1964 (s) $cm^{-1}$; $^1$H NMR: δ 7.86-7.43 (m, Ar-$\underline{H}$). $^{13}$C NMR: δ 196.9 (-$\underline{C}$OPh), 145.4 ($\underline{C}$-$CS_2$), 137.6-125.7 (other Ar); ESMS: (MeOH with added Na[OMe], cone voltage 10 V), m/z 455 (40%) $[M+OMe]^-$; 427 (100%) $[M+OMe-CO]^-$; 653 (78%) $[2M-Mn(CO)_5]^-$.

### *2.3.3 Reaction of $\eta^2$-(2-acetylthien-3-yl)tetracarbonylmanganese with $CS_2$.*

The cyclomanganated thiophene derivative (112 mg, 0.38 mmol) was reacted with $CS_2$ (*ca* 10 mL) in a sealed ampoule at 85°C for 24 h, as above. Excess $CS_2$ was removed and the residue recrystallised from dichloromethane: petroleum spirits at -20°C. Dark yellow rods of $\eta^2$-(2-acetyl--thien-3-yl-dithiocarboxylato)tetracarbonylmanganese, **6**, were obtained (114 mg, 80%). Mp 108°C (dec.) Found: C 36.1; H 1.4%. Calc. for $C_{11}H_5MnO_5S_3$: C 35.9; H 1.4%. IR: ν(CO) ($CH_2Cl_2$) 2093 (m), 2016 (vs, br),1966 (s) $cm^{-1}$; $^1H$ NMR: δ 7.45 (1H, d, $^3J_{H\text{-}H}=5.0$ *Hz*, Ar-$\underline{H}$), 7.24 (1H, d, $^3J_{H\text{-}H}=5.0$ *Hz,* Ar-$\underline{H}$), 2.66 (3H, s, -C(O)C$\underline{H}_3$). $^{13}C$ NMR: δ 191.4 (-$\underline{C}$(O)$CH_3$), 150.4 (Ar), 140.0 (Ar), 129.8 (Ar-H), 128.4 (Ar-H), 30.0 (-C(O)$\underline{C}H_3$). ESMS: (MeOH with added Na[OMe], cone voltage 10 V), m/z 399 (68%) $[M+OMe]^-$; 371 (74%) $[M+OMe-CO]^-$; 339, (16%) $[M-CO-H]^-$ ; 541 (100%) $[2M-Mn(CO)_5]^-$.

### *2.3.4 Reaction of $\eta^2$-[(2-diphenylthiophosphinyl)phenyl] tetracarbonylmanganese with $CS_2$.*

Cyclomanganated triphenylphosphine sulfide **2b** (125 mg, 0.31 mmol) was reacted with $CS_2$ as above. $^{31}P$ NMR and ESMS on the crude reaction mixture showed the presence of the starting material **2b** and $Ph_3PS$. Excess $CS_2$ was removed and the residue recrystallised from $CH_2Cl_2$: $Et_2O$ at -20°C. A small yield of orange blocks were obtained, identified as $(\mu_3\text{-}CS_3)_2Mn_4(CO)_{16}$ **7**. Mp >115°C (dec.) Found: C 23.5; H 0.0%. Calc. for $C_{18}Mn_4O_{16}S_6$: C 24.5; H 0.0%. IR: ν(CO) ($CH_2Cl_2$) 2091 (s), 2049 (m), 2009 (vs, br), 1979 (m), 1965 (m) $cm^{-1}$; ESMS: (MeCN, cone voltage 10 V), m/z 717 (100%) $[M-Mn(CO)_4]^-$; 689 (27%) $[M-Mn(CO)_4-CO]^-$; 661, (8%) $[M-Mn(CO)_4-2CO]^-$. The characterisation was confirmed by an X-ray crystal structure analysis; see below.

Similar reactions of orthomanganated triphenylphosphine selenide (**2c**), orthomanganated triphenylphosphine phenylimine (**2a**)and the orthomanganted chalcone (**3a**), also gave low yields of $(\mu_3\text{-}CS_3)_2Mn_4(CO)_{16}$ as the only carbonyl-containing product.

### *2.3.5 Reaction of dimanganese decacarbonyl with $CS_2$.*

$Mn_2(CO)_{10}$ (517 mg, 1.33 mmol) was reacted with $CS_2$ in a sealed ampoule at 110°C for 24 h. The unopened ampoule was stored at -20°C for 48 h, to give crystals of the crude product. These were collected by filtration and chromatographed on silica gel plates, eluting with $CH_2Cl_2$:petroleum spirits (1:1) to give as the major product $(\mu_3\text{-}CS_3)_2Mn_4(CO)_{16}$, **7**, (217 mg, 39%). Spectroscopic data was identical to that given in 2.3.4.

### *2.4 X-ray crystallography.*

For compound **7** unit cell parameters and intensity data were collected using a Siemens SMART CCD diffractometer, using standard collection procedures, with monochromatic Mo-Kα X-rays (0.71073 Å), while for **4** a Siemens P4 four-circle diffractometer was used. Corrections for absorption and other effects were carried out with SADABS [16]. All other calculations used the SHELX97 programs [17]. The structures were solved by direct methods, and developed routinely with refinement based on $F^2$. All non-hydrogen atoms were assigned anisotropic temperature factors, and hydrogen atoms were included in calculated positions.

#### *2.4.1 Crystal data for $\eta^2$-(2-acetyl-5-methoxyphenyldithiocarboxylato)tetracarbonylmanganese(**4**)*

$C_{14}H_9MnO_6S_2$, $M_r$ 392.27, orthorhombic, Pnma, a = 22.878(8), b = 7.005(3), c = 9.973(6) Å, V = 1598.1(14) Å$^3$, $D_{calc}$ = 1.630 g cm$^{-3}$, Z = 4, F(000) = 792, μ(Mo-$K_\alpha$) 1.113 mm$^{-1}$, $T_{max}$ 0.262, $T_{min}$ 0.238, crystal size 0.66 x 0.17 x 0.04 mm$^3$. T 168 K.

A total of 1999 reflections, 1364 unique ($R_{int}$ 0.0407) was collected 2° < θ < 24°. Final $R_1$ 0.0415 [data with $I > 2\sigma(I)$], 0.0767 (all data), $wR_2$ 0.0863, GoF 1.014, final Δe +0.37/-0.35.

The structure is illustrated in Figure 1, while selected bond parameters are listed in the caption.

#### *2.4.2 Crystal data for $(\mu_3\text{-}CS_3)_2Mn_4(CO)_{16}$. (7)*

$C_{18}Mn_4O_{16}S_6$, $M_r$ 884.30, triclinic, $P\bar{1}$, a = 7.010(3), b = 8.410(4), c = 13.674(6) Å, α = 83.40(1), β = 80.04(1)°, γ = 74.21(1), V = 762.1(5) Å$^3$, $D_{calc}$ = 1.927 g cm$^{-3}$, Z = 1, F(000) = 432, μ(Mo-$K_\alpha$) 2.099 mm$^{-1}$, $T_{max}$ 1.00, $T_{min}$ 0.76, crystal size 0.26 x 0.16 x 0.05 mm$^3$. T 168 K.

A total of 9436 reflections, 3016 unique ($R_{int}$ 0.0333) was collected 2° < θ < 26.5°. Final $R_1$ 0.0309 [data with $I > 2\sigma(I)$], $wR_2$ 0.0702, GoF 0.954, final Δe +0.63/-0.50. The structure is illustrated in Figure 2, with selected bond parameters in the caption.

## 3. Results and Discussion

The reaction of the cyclometallated acetophenone **1** with $CS_2$ at 85°C for 24 h gave a reasonable yield of the dithiocarboxylate complex ($\eta^2$-$MeOC_6H_4CS_2$)$Mn(CO)_4$, **4**, which crystallised on cooling the reaction mixture. The temperature of reaction was critical; below 80°C little change took place while above 90°C extensive decomposition occurred.

[Diagrams 4-8 near here]

The new complex **4** showed in the IR spectrum a characteristic νCO pattern for a *cis*-$L_2Mn(CO)_4$ species, with a shift of around 10 $cm^{-1}$ to higher frequencies compared with the starting complex **1**. The $^1H$ and $^{13}C$ NMR spectra were consistent with the dithiocarboxylate structure. Similarly the electrospray mass spectrum, with Na[OMe] added as an ionisation aid [15], gave expected peaks arising from both $OMe^-$ addition and $H^+$ abstraction from **4**. However the spectroscopic data did not completely distinguish between the $\eta^2$-$RCS_2$ bonding pattern as in **4**, and an alternative which has an $\eta^1$-$RCS_2$ with the >C=O of the acetyl group still coordinated, as in **8**. Therefore a single crystal X-ray determination was carried out to distinguish between the two possibilities.

The structure is illustrated in Figure 1. It shows that structure **4** is adopted, with the $Mn(CO)_4$ group attached to the organic ligand by a symmetrical $\eta^2$-$RCS_2$ linkage. The $CS_2$ group is orthogonal to the aryl plane of the rest of the ligand, and the C=O group is uncoordinated. As expected, the Mn-CO distances of the two CO ligands *trans* to each other are significantly longer than the Mn-CO bonds *trans* to the dithiocarboxylate ligand.

The corresponding reactions of orthomanganated benzophenone, and the orthomanganated 2-acetylthiophene complex, with $CS_2$ under the same conditions produced the equivalent dithiocarboxylate complexes **5** and **6** respectively. This suggests that for manganated aryl ketones the conversion of the C,O-bonded R ligand to a $RCS_2$ ligand is general.

A suggested pathway to **4-6** in these reactions involves initial insertion of $CS_2$ into the Mn-C bond to give a S,O-bonded ligand with a seven-membered chelate ring, as in **8**. Displacement of the O-donor by the second sulfur atom would give the final product. This pathway is consistent with reactions of orthomanganated complexes involving other unsaturated molecules.

Although compounds **4-6** are new examples, other dithiocarboxylate complexes of $Mn(CO)_4$ are established, having been prepared previously by insertion of $CS_2$ into the Mn-C bond of $RMn(CO)_5$ compounds [12]. This earlier method, however, gave much lower yields (1-17%) than those found in the present study for the cyclomanganated substrates (55-80%). There appears to be only two instances of the direct reaction of dithiocarboxylate anions with either $BrMn(CO)_5$ or $[Mn(CO)_5(MeCN)]^+$ to give related species [18]. Therefore the reaction of $CS_2$ with orthomanganated aryl ketones may provide a useful route to dithiocarboxylates, especially those with functional groups that would interfere with the other syntheses.

The reaction of $CS_2$ with orthomanganated triphenyl phosphine sulfide, **2b**, was also investigated. This gave no evidence for the formation of a dithiocarboxylate, with the only new carbonyl-containing product being dark-yellow crystals isolated in low yield. Spectroscopic and analytical data were inconclusive, so an X-ray structure determination was carried out. This showed the product to be **7** as illustrated in Figure 2. The centrosymmetric molecule consists of two $\eta^3$-trithiocarbonate anions, each with two of the sulfur atoms chelating to a $Mn(CO)_4$ group, while the third acts as a bridging atom between two other $Mn(CO)_4$ groups. The $CS_3^{2-}$ groups are planar, with shorter C-S bonds to the chelating S atoms (1.695 Å) than to the bridging one (1.763 Å). The pyramidality at the bridging S atom induces a Z shape to the molecule (see inset to Figure 2). The overall molecule is a combination of two common motifs -- $(\eta^2\text{-}RCS_2)Mn(CO)_4$ as in the dithiocarboxylates discussed above [12, 18] and related species [19], and a $(\mu\text{-}SR)_2Mn_2(CO)_8$ unit which is well-known for manganese carbonyl thiolates [20].

Also related to compound **7** are the $[(\eta^2\text{-}CS_3)Mn(CO)_4]^-$ and $(CO)_5Mn(\eta^3\text{-}CS_3)Mn(CO)_4$ complexes found by Benson *et al* in reactions of $[Mn(CO)_5]^-$ with $CS_2$ [21].

Compound **7** does not appear to have been reported before, but the isomorphous Re analogue was isolated from the reaction of $F_3CRe(CO)_5$ with $CS_2$ [12, 22]

The route to **7** is not clear. It seemed possible that the third S atom might have come from the orthomanganated $Ph_3P{=}S$, but this was discounted when **7** was also the product (albeit in low yield) when using the corresponding orthomanganated $Ph_3P{=}Se$ (**2c**); ESMS of the crude reaction mixture showed no traces of a dithioselenocarbonate analogue of **7** which would have been expected if atom transfer from the phoshine chalcogenide was involved.

Similarly $Ph_3P{=}NPh$ (**2a**) and chalcone (**3**) gave low yields of **7** when they were reacted with $CS_2$ under the same conditions.

To find a more rational synthesis of **7**, $Mn_2(CO)_{10}$ was reacted with $CS_2$. Although a higher temperature was needed (110°C) the isolated yield of **7** was reasonable, 39%. It seems that formation of $CS_3^{2-}$ ligands can readily arise from a formal redox disproportionation of $CS_2$ in reactions of a variety of manganese [21] (or rhenium [22] or nickel [14]) compounds.

## 4. Supplementary material.

Crystallographic data for the structural analyses have been deposited with the Cambridge Crystallographic Data Centre, CCDC no xxxxxx for **4** and **7** respectively. Copies of this information may be obtained free of charge from the Director, CCDC, 12 Union Rd., Cambridge CB2 1EZ, UK (Fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

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## Captions to Figures

Figure 1. The structure of $\eta^2$-(2-acetyl-5-methoxyphenyldithiocarboxylato)tetracarbonylmanganese **4**. Bond parameters include: Mn(1)-S(1) 2.381(1), S(1)-C(1) 1.676(3), Mn(1)-C(11) 1.815(5), Mn(1)-C(12) 1.869(7)Å; S(1)-Mn(1)-S(1') 72.73(6)°, Mn(1)-S(1)-C(1) 86.2(2)°, S(1)-C(1)-S(1') 114.7(3)°.

Figure 2. The structure of $(\mu_3\text{-}CS_3)_2Mn_4(CO)_{16}$ **7**. Bond parameters include: Mn(1)-S(1) 2.3866(11), Mn(1)-S(2) 2.3971(13), Mn(2)-S(3) 2.4035(13), C(1)-S(1) 1.691(3), C(1)-S(2) 1.699(3), C(1)-S(3), 1.763(3) Å; S(1)-Mn(1)-S(2) 73.18(3)°, Mn(2)-S(3)-Mn(2') 100.18(3)°, S(3)-Mn(2)-S(3') 79.82(3)°, Mn(1)-S(1)-C(1) 86.41(10)°, S(1)-C(1)-S(2) 114.52(16)°, S(1)-C(1)-S(3) 122.84(16), S(2)-C(1)-S(3) 122.53(16)°. The inset is a side view emphasising the Z-shape of the molecule.

**Synopsis**.

Cyclomanganated aryl ketones react with $CS_2$ to generate dithiocarboxylate complexes of $Mn(CO)_4$.